Full Length Article

Performance of Mn-based H$_2$S sorbents in dry, reducing atmosphere – Manganese oxide support effects

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Svatopluk Chytil [a,*], Milly Kure [b], Rune Lødeng [a], Edd A. Blekkan [b]

[a] SINTEF Materials and Chemistry, Department of Kinetic and Catalysis, Postbox 4760, Sluppen, N-7465 Trondheim, Norway
[b] Department of Chemical Engineering, Norwegian University of Science and Technology (NTNU), N-7491 Trondheim, Norway

HIGHLIGHTS

- Additive effect observed for cerium supported manganese oxide due to H$_2$S sorption on the support as well as on the Mn oxide.
- Superior stability of zirconium supported Mn oxide in H$_2$.
- Strong metal oxide-support interaction influences the sorbent performance.

ARTICLE INFO

ABSTRACT

High temperature H$_2$S sorbents comprising manganese oxide (15 wt.%) supported on TiO$_2$, ZrO$_2$, CeO$_2$ and Al$_2$O$_3$ were prepared by wet impregnation using Mn(NO$_3$)$_2$·4H$_2$O as Mn precursor. Upon activation in H$_2$, the sorbent performance testing was conducted at 650 °C in a model gas mixture with a composition of 0.4 vol.% of H$_2$S in 40 vol.% of H$_2$, the balance being inert gas. Sorbent regeneration was performed at 650 °C with 5.2 vol.% of O$_2$ in N$_2$. The initial sorption performance is first reported for the parent (Mn-free) supports showing a considerable H$_2$S sorption on ZrO$_2$ and CeO$_2$ and a minor sorption on Al$_2$O$_3$ and TiO$_2$. The Mn sorbents were subject to 13 sorption/regeneration cycles. The highest initial sorption capacity is reported for cerium supported Mn oxide, which is also the sample that deactivates most. A prolonged exposure to H$_2$ at 650 °C results in a reversible loss of the sorption capacity that was observed for all the samples except for Mn on zirconia suggesting its superior stability in H$_2$.

The supports, fresh and regenerated Mn sorbents were characterized by means of N$_2$ sorption measurements, X-ray Diffraction and Raman spectroscopy. Temperature-Programmed Reduction was performed on the parent supports and fresh sorbents. The changes in material properties caused by the testing as well as a different degree of a metal oxide-support interaction influencing the sorption performance are discussed.

1. Introduction

The product gas from gasification termed as a producer gas contains besides the main components (H$_2$, CO, CO$_2$, CH$_4$, C$_2'$s, N$_2$, H$_2$O) some impurities such as dust, tar, NH$_3$, H$_2$S, COS, HCl and some trace elements (e.g. alkaline and alkaline metal earth metals and other inorganics) [1–3]. If the use of the producer gas requires advanced materials (e.g. catalyst) or fuel cells, the impurities need to be removed or reduced down to a very low level. For some applications as low concentrations as 60 ppb have been reported to be necessary [4]. In the case that the gas is to be used in the Solid

Oxide Fuel Cell technology or in the Fischer-Tropsch synthesis utilizing Co based catalyst, the required H$_2$S limits typically are reported to be 1 ppm [5,6].

Achieving such low concentrations is possible by solvent based absorption methods. However, the processes may lower the thermal efficiency due to cooling and subsequent reheating of the gas and the investment cost is often too high [7–9]. The use of solid sorbents has become increasingly important in biomass based process where the capacity of the plant is fairly small.

Mn oxides are together with Zn- and Fe-based sorbents often studied as suitable candidates for the H$_2$S removal from the producer gas. However, the high temperature can induce a formation of carbides and metallic Zn for the Fe and Zn oxides respectively [7,8]. This may suppress the sorbent capacity and even cause some problems in the downstream processing. It has also been reported

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that the H_2S sorption kinetics, which is one of the key parameters when choosing a suitable sorbent, is more favorable for the Mn oxides when compared to the Zn ones [10].

An important aspect when selecting a sorbent is its durability and stability under the reaction conditions. In a recent work, performed with a model producer gas and using Mn_xO_y-Al_2O_3 sorbents, some performance decay over multiple sorption/regeneration cycles was observed [11]. As it was suggested that the use of alumina may be partly responsible for the deactivation, the use of other supports for the Mn oxide was examined. In this contribution we first present H_2S sorption data obtained for the parent supports in order to clarify whether the supports themselves are capable of removing H_2S from the model gas mixture under the experimental conditions used. The sorption performance for Mn oxides supported on CeO_2, ZrO_2 and TiO_2 are then compared to the performance of Mn_xO_y-Al_2O_3 and also considering the performance of the parent support.

Characterization by means of fundamental methods is also presented here which allows evaluating the material properties relevant for the sorption as well as the change of the properties upon the multiple sorption/regeneration cycles. A particular attention is also devoted to the interaction between the support material and Mn as it is reasonable to expect that it may influence the sorbent performance.

2. Experimental

2.1. Chemicals

All chemicals and gases were used as received without further purification. The γ – alumina support LOT# B5160010 and purity 96% was obtained from Strem chemicals. $Mn(NO_3)_2\cdot4H_2O$ purum p.a. and Titanium (IV) oxide *puriss* was purchased from Sigma Aldrich. Zirconium oxide LOT#J10T008 was received from Alfa Aesar. Cerium (III) nitrate hexahydrate, 99.99% metal basis was purchased from Sigma Aldrich.

2.2. Sample preparation

As-received alumina was calcined in an oven under static air conditions at 500 °C for 10 h prior to its functionalization with Mn. The CeO_2 support was obtained by the heating of the cerium nitrate precursor in an oven under air static conditions at 600 °C for 10 h [12]. As-received TiO_2 was also treated in air under static conditions at 700 °C for 10 h prior to its impregnation with the Mn salt in aqueous solution [13].

The manganese sorbents were prepared by the wet impregnation method using the Mn nitrate precursor, the parent supports and deionized water. Following the impregnation, the samples were dried at 100 °C for 24 h. Calcination of the samples was performed at 600 °C in static air for a period of 5 h. The heating rate used was 1 °C/min. The nominal Mn loading was 15 wt.%. The sorbent samples are assigned with a prefix Mn15 followed by the support name used; e.g. Mn15-Al_2O_3. The regenerated samples after the multiple sorption/regeneration cycles are denoted with an affix –R; e.g. Mn15-Al_2O_3-R.

2.3. Instrumentation

Nitrogen adsorption-desorption isotherms were measured using a Micromeritics TriStar 3000 instrument. Prior to the measurement, the samples were outgassed at 100 °C for 12 h. The specific surface area of the solids was evaluated by the BET method (Brunauer-Emmett-Teller) in the range of relative pressures $p/p_0 = 0.1$–0.3. The pore size distributions were obtained from the adsorption branch of the isotherm using the Broekhoff – De Boer algorithms [14].

X-ray diffraction analysis (XRD) of the solid materials were performed on a Bruker AXS D8 Focus diffractometer using CuK_α radiation ($\lambda = 1.54$ Å).

Raman spectroscopy measurements were performed on a Horiba Jobin Yvon, LABRAM HR 800 instrument. A laser excitation source of 633 nm was used and focused with a 50× objective.

TPR measurements were performed on an in-house built apparatus [15]. Typically, the sample was heated in the temperature range 50–850 °C using a heating rate of 10 °C/min. For the CeO_2 and Mn15-CeO_2 sample, an extended temperature range 50–1000 °C was used. The reduction behavior of the samples was measured in a gas mixture consisting of 7 vol.% of H_2 in Ar.

The laboratory set-up used to measure the sorption-regeneration cycles consists of a gas feeding and metering system, a quartz fixed bed reactor and an analytical section. The set-up is described in detail elsewhere [11]. The gas concentrations are measured continuously by a ThermoStar GSD 320 T1 C analytical system equipped with a quadruple mass spectrometer QMS 200 using a secondary electron multiplier (SEM) or Faraday cup detector. The set-up was used without any significant modification. However, an additional thermocouple was installed on the external wall of the quartz rector in order to monitor the changes of the reactor temperature.

Prior to the sorption experiment, the sample was reduced in-situ in the H_2/N_2 mixture (50 ml/min) during the heating to the reaction temperature and then for approximately one hour before the sorption experiments. The system was then flushed with N_2. Consequently, the sorption gas was introduced first to the bypass and when the concentration of all the presented species was stable (as monitored by the MS), the sorption gas was directed to the reactor.

The feed gas composition for the sorption was 0.4, 39.6, 40.0 and 20 vol.% for H_2S, Ar, H_2 and N_2 respectively. A rather high H_2S concentration was used in order to facilitate a large number of sorption/regeneration cycles during the testing period. The sorbent regeneration was conducted in a gas mixture containing 5.2 vol.% of O_2 in N_2. The total gas flow used for the sorption and regeneration was 50 ml/min and the sample mass was 0.1 g. The concentration of the components present in the sorption gas was measured quantitatively as based on a regular calibration of the MS. However, the O_2 and SO_2 concentration during the regeneration was monitored only qualitatively following the m/z values of O_2 and SO_2. N_2 contained in the model gas mixture was used as an internal standard to calibrate the MS, while the second inert gas Ar diluted H_2S in the supplied gas mixture (1 vol.% H_2S in Ar).

The sorption and regeneration were performed at 650 °C and 101.325 kPa. The sorbent particle size was typically in the range 150–250 μm and it was not diluted with any additional solids. The length of the sorbent bed was approximately 4 mm and the reactor inner diameter was 6 mm. In total 13 sorption/regeneration cycles were performed for each sorbents sample while 1–2 cycles were performed on the parent supports. The parent supports were activated/pretreated in the reducing atmosphere in the same manner as the Mn containing sorbents. For the Mn sorbents, the first and the thirteenth sorption cycle were run until complete sorbent saturation while the remaining sorption cycles were terminated when a H_2S concentration of 0.1 vol.% in the outlet was reached. In between each sorption/regeneration cycle the system was flushed with N_2. During the longer breaks between the cycles (overnight), the system was kept under N_2/H_2 flow at the reaction temperature. The total flow in that case was 20 ml/min and the composition was the same as used for the activation i.e. 50 vol.% of H_2 in N_2. Afterwards, an increased flow of 50 ml/min of the same gas mixture was used for approx. 1 h. The system was then flushed